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A STUDY OF THE SODIUM-HYDROGEN-OXYGEN SYSTEM.(U)
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A STUDY OF THE SODIUM-HYDROGEN-OXYGEN SYSTEM.

by

Dale D. Williams
Chemistry Division

June 1952

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Approved by: R. R. Miller, Head, Physical and Inorganic Branch
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ABSTRACT

The sodium-hydrogen-oxygen system has been investigated in continuation of the study of impurities in liquid metals.

Sodium metal reacts with sodium hydroxide at temperatures above 300°C to form sodium monoxide and sodium hydride. If the reaction is initiated in vacuo, hydrogen will be liberated to the extent of the dissociation pressure of sodium hydride at temperatures below 385°C. If this hydrogen is not removed from the reaction zone, and if the temperature is raised beyond 385°C, an equilibrium is established which does not follow the dissociation pressure diagram for sodium hydride. This new equilibrium appears to be related to the solubility of the reaction products in sodium metal and in sodium hydroxide. The "keystone" of the equilibrium appears to be the fusion temperature of the melt which, in turn, is determined principally by the ratio of sodium monoxide to sodium hydroxide.

Data are presented showing that the dissociation of sodium hydride is suppressed by an inert gas blanket. It is indicated that sodium hydride must vaporize or sublime before it will dissociate. It is further shown that sodium hydride in solution is quite stable, even in vacuo at temperatures well above those at which the hydride should be dissociated.

Data for the potassium-hydrogen-oxygen system are entirely different from that reported for the corresponding sodium system. The difference could well be related to a higher solubility of the reaction products in the reactants.

PROBLEM STATUS

This is a preliminary report on this subject and work will be continued in connection with the study of solubility of impurities in liquid metals.

AUTHORIZATION

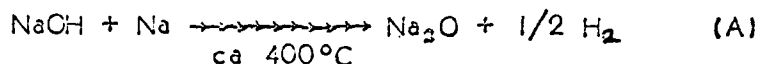
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INTRODUCTION

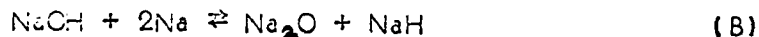
Results which have been collected in connection with the study of impurities in alkali metals are presented along with attempts to explain the physical states contributing to these data. While data are not yet available to establish the physical states with exactness the results are considered to be of sufficient value to those working in this field to report the information acquired. The application of the phase rule to explain the results required that somewhat dubious assumptions be made concerning the phases and components which are under question.

In continuation of the study of the effect of impurities in sodium metal (1 and 2), the sodium-hydrogen-oxygen system has been examined. The compounds resulting from combinations of these elements would include sodium monoxide, sodium hydroxide, sodium hydride, water, hydrogen, sodium metal and oxygen. The water and oxygen would, of course be of a transient nature in any mixture involving sodium metal, but might, under certain conditions, exist for a sufficient length of time to be identifiable. The peroxide and superoxide of sodium were not considered since they are readily reduced to the monoxide by the action of metallic sodium.

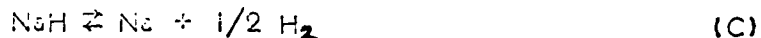
Pepkowitz and Judd (3) and Pepkowitz and Proud (4) report the reduction of sodium hydroxide by sodium metal according to equation (A)



The method reported in (4) does not allow for the reversibility of this reaction and the assumption of its validity in (3) does not allow for the stability of sodium hydride in solution (6). The reaction could, therefore, proceed according to equation (B)



Equation (C)



might then result in whole or in part depending upon the solubility of sodium hydride in the reaction medium, and upon whether the conditions of the experiment allowed for the escape of the evolved hydrogen. Halla and Tompa (5) report the validity of equation (B) for the reaction of metallic sodium with fused sodium hydroxide. Gilbert (6) reports two methods for preparing a solution of sodium hydride in fused sodium hydroxide.

Both of his methods involve the passing of hydrogen through fused caustic containing, in one case, sodium metal, and in the other, sodium monoxide. It seems likely, therefore, that some equilibrium exists whereby it is possible to have sodium, sodium hydroxide, sodium monoxide, sodium hydride and hydrogen co-existing in a reaction vessel.

A complete investigation of this system is hampered by nearly insurmountable analytical problems. It was found that the equilibrium shifts quite rapidly; hence, any attempt to "freeze" the reaction at some high temperature level is defeated from the start. Further, any attempt to separate any one of the reactants for individual analysis results in equilibrium shifts of such moment as to defeat the purpose of the separation. However, substantial evidence as to possible reactions and/or equilibria is afforded by the pressure of evolved hydrogen in a calibrated volume, subsequent analysis of total reaction products and control of original weights of reactants.

Apparatus and Method

The apparatus (Figure 1) consisted of a metal "pot" equipped with a metal ball-joint. This was connected, through a complementary glass socket joint and a stopcock to a pyrex system consisting of a calibrated flask and a differential manometer. An outlet for connection to a high vacuum, inert gas manifold was also provided. The heat source was a helical coil nichrome heater furnace controlled by a variable transformer. Temperature readings were made with a chromel-alumel thermocouple and both a Hoskins pyrometer and a Brown recording potentiometer. The accuracy of the temperature readings is $\pm 5^\circ\text{C}$ through 500°C and decreases to $\pm 10^\circ\text{C}$ at 700°C . Pressures were read to the nearest millimeter and all readings were converted to STP conditions.

The sodium hydroxide used was c.p. material with individual analyses falling within the following ranges:

NaOH -----	95-97%
Na ₂ CO ₃ -----	1-2%
H ₂ O -----	2-3%

The water was readily removed by heating the hydroxide to its fusion point under vacuum. In some cases the water was removed by adding metallic sodium at 125°C and pumping away the evolved hydrogen. The material could be thus dried at a much lower temperature than by heat and vacuum alone. The carbonate content of the hydroxide was ignored in considering the equilibrium reactions since, in all runs reported herein, the carbonate was

apparently unaffected and was recovered as such in the re-action products. Recoveries were, in all cases, exactly what was added in the original charge. Any effect of carbonate as a catalyst or a carrier for some of the reactions reported is beyond the scope of this report.

Metallic sodium for the experiments was cut from duPont air cast brick, melted, filtered and stored in pyrex flasks. Known volumes were introduced into the apparatus by pipetting under an inert gas blanket, usually nitrogen.

The sodium hydride used was obtained from duPont and analysed 98% NaH, the remainder being metallic sodium and sodium hydroxide.

The sodium monoxide was made by reacting sodium hydroxide with metallic sodium in a high vacuum and subsequently removing the excess sodium metal by distillation. The material analysed 98.8% Na₂O, 1.1% Na₂CO₃ with spectrographic traces of Cr and Fe.

The metal "pot" on the apparatus was made originally of type 304 stainless steel and later of recast commercial grade nickel having the following analysis --

Ni	98.74%
Co	0.20
Fe	0.63
Mg	0.21
Mn	0.11
Cu	0.05
Si	0.015
Cr	trace
C	0.012

The change to nickel was made following the discovery of attack on the stainless steel at temperatures above 600°C. There was no evidence of attack below this temperature. Nickel was unaffected to a temperature of 700°C. As will be shown, the attack on stainless steel does not affect the experiments herein reported. Duplicate runs in stainless and nickel are identical for temperatures up to 600°C.

Runs were made using two different calibrated volumes, one approximately twice as large as the other. Data from both type runs proved that the amount of "dead space" in the system had no effect on the reaction except as to the quantity of reactants necessary to produce a given pressure in the different volumes.

The method of operation was essentially the same for all runs. The reactants were introduced into the apparatus, the

system was evacuated and heat applied. Temperature-pressure relationships were obtained for the temperature range desired or until no further reactions occurred -- indicated by a cessation of hydrogen evolution or absorption. The apparatus was then cooled and the "pot" cut open if analysis of the total reaction products was desired. (In some cases, reaction products were recovered following removal of excess sodium metal by vacuum distillation.)

Figure 2 is a plot of data obtained to show the effect of sodium hydroxide on the container materials used in the experiments. As may be seen, stainless steel - type 304 is not attacked at temperatures below 600°C and nickel not below 700°C. (Care was taken during welding operations to prevent oxidation on the interior of the pot, a condition which would have led to a certain amount of attack from the reductions of the oxides.) Figure 2 also contains a plot of the stainless steel "pot" with H₂ added to 425 mm pressure, heated through the same temperature range. As shown, little or no hydrogen is absorbed by the vessel at these temperatures. The slight absorption at the higher temperature is accountable for by reduction of surface oxides.

Results

It was determined that sodium did react with sodium hydroxide yielding sodium monoxide and hydrogen. The reaction would go to completion, however, only if the hydrogen was removed from the reaction zone.

Figure 3 shows the type of curve obtained by heating sodium hydroxide and sodium metal through the stated temperature range without removing hydrogen. The curve is typical of that obtained for all proportions of metal and hydroxide studied wherein hydroxide in an amount sufficient to provide ca 200 mm hydrogen pressure was present. The general shape of the curve is the same for hydroxide in less than this amount, but the "breakaway" from the first part of the curve occurs at a lower temperature and the peak pressure obtained at 425°C is lower. Figure 4 shows the amounts of sodium hydroxide required, with an excess of sodium, to obtain various peak pressures. The rise in pressure above 600°C is seen from Figure 2 to result from attack on the stainless steel "pot" and, possibly, further direct release of hydrogen from the hydride.

It should be here emphasized that the "dome-shaped" plateau and the reabsorption dip in Figure 3 occurred at the same pressures and temperature even when there were sufficient reactants present to give pressures much higher than the peak shown. In no case involving the reaction of sodium with sodium hydroxide was a pressure greater than 195 mm obtained. A range of 1/4 through 8/1 sodium/sodium hydroxide ratios were

examined with identical temperature-pressure relationships resulting.

Examination reveals that the first portion of the curve (up to 385°C) is in excellent agreement with the dissociation pressure of sodium hydride as reported by Keyes (7) and by Herold (8). (Their work was repeated by the author as a check on his method and apparatus. Figure 5 contains this comparative data.) The pressures obtained at these temperatures (up to 385°C) seem to be true equilibrium points in that, if conditions are shifted by removal of the hydrogen, the same pressure will be obtained repeatedly until all sodium hydroxide has been converted to sodium monoxide. However, at higher temperatures (at and above the temperature of peak pressure, 425°C), the pressure readjustment is dependent upon the quantity of reactants remaining in the pot. For example, a run begun with 9 grams of sodium hydroxide (sufficient to give a hydrogen pressure of 900 mm) and heated to 425°C returned to 180-190 mm three times following hydrogen removal, then, successively, to 169mm, 112mm, 52mm, and 26mm. This lowering of equilibrium pressure following successive evacuations was typical of all runs at temperatures above 385°C. This effect will later be shown to be allied to stability of the hydride in solution as well as the manner in which it is dispersed in the melt. Figure 4 shows the peak equilibrium pressure obtained at ca 425°C plotted against the original quantity of sodium hydroxide. This figure also shows that the size of the "dead space" has no effect upon the peak pressure obtained. A similar plot of sodium metal against pressure shows no correlation whatsoever.

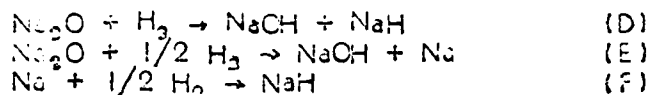
A peak pressure of ca 190mm is always obtained on heating. However, if the run be continued so as to obtain the minimum pressure shown at about 550°C, then cooled, the cooling curve pressure returns linearly until a temperature of ca 385°C is reached and then tends to fall along the heating curve. (Figure 6). It would follow then that the "hump" is but a quasi-equilibrium resulting from two or more competing reactions. This will later be shown to be true.

An interesting phenomena was discovered in a series of runs made under various pressures of inert gases. It was hoped that distillation of the metallic sodium at the higher temperatures could be reduced by the use of an inert gas blanket. This should not, it was thought, affect the partial pressure of hydrogen evolved from the reaction. Figure 7 shows the results of two runs made under 760mm and 380mm of nitrogen. The evolution of hydrogen is seen to have been nearly completely suppressed except at temperatures above 600°C. Hydrogen evolution at this

temperature apparently resulted from attack on the stainless steel vessel rather than hydride dissociation. The same experiment was repeated using sodium hydride alone with very similar results (Figure 7). A further sodium hydride run was made under conditions whereby the sample was heated to 410°C under 760mm of nitrogen, then successive portions of the inert gas removed and partial pressures of hydrogen and nitrogen observed. The data from this run are shown in Figure 8. As may be seen, the dissociation pressure of sodium hydride is evidently a function of total system pressure rather than one of hydrogen partial pressure alone. The same experiment with exactly the same results was performed with a sodium hydroxide-sodium metal melt. No hydrogen was evolved until the total pressure was reduced to below 185mm. These data are also shown in Figure 8. The effect of inert gas on the dissociation of sodium hydride is not a reversible process. Once hydrogen has been evolved, additions of inert gas do not cause readjustment of the system pressure.

It would appear from the foregoing that sodium hydride must vaporize or sublime before it will dissociate. This fact would also account, in part, for its remarkable stability when in solution. An experiment was designed to further substantiate this assumption. A small flask was equipped with a manometer, sodium hydride added and heat applied. At a temperature of 190°C the pressure rose perceptibly, at the same time a silver mirror was deposited well up on the walls of the flask. Subsequent analysis proved the film to be sodium metal. Sodium metal heated similarly did not deposit this film at these temperatures. The flask was then equipped with a cold finger constructed in such a manner as to cover the exposed surface of the sodium hydride. As heat was applied, with the flask under high vacuum, the particles of sodium hydride became extremely agitated and crystals of the hydride were collected on the cold finger. There was little or no rise in pressure accompanying this collection. Next, a pressure of 10mm of nitrogen was introduced. Both the agitation and the crystal growth ceased instantly. Further substantiation of this phenomena was provided in later experiments with small amounts of sodium hydride in sodium hydroxide in which hydrogen should have been released both from the dissociation of the sodium hydride and from subsequent reaction of the sodium metal thus produced with the hydroxide. This was found not to be the case; the hydrogen equivalent to the decomposition of sodium hydride being all that was recovered. This indicated that the sodium metal must have been removed from the reaction zone before it could react with the hydroxide. Vaporization or sublimation of the sodium hydride prior to dissociation would have resulted in such a reactant separation.

Further evidence of the availability of sodium hydride as a component of the sodium-sodium hydroxide system is afforded by the reaction of sodium monoxide with hydrogen. This reaction has been demonstrated in fused caustic by Gilbert (6). The author has substantiated Gilbert's results in the dry state. Figure 9 shows the reaction of hydrogen with sodium monoxide. The points shown are not equilibrium points, but show the effect of a constantly increasing temperature. The reaction proceeds at temperatures as low as 175°C and the resulting hydride and hydroxide are stable at temperatures as high as 425°C. The reaction could proceed according to one or more of the following equations --



If it were to proceed by only equation (E), 1/2 mole of hydrogen would be consumed per mole of monoxide; and if by only equation (D), one mole of hydrogen per mole of monoxide. In the experiment plotted in Figure 9, 2.76 grams of Na_2O consumed 940 ml of hydrogen. This is 94% of the theoretical quantity required to satisfy equation (D) and 188% of that required for equation (E). A combination of equations (E) and (F) is, in effect, equation (D). However, under the static conditions prevailing in his apparatus, the author has been unable to produce more than a few milligrams of sodium hydride by the direct reaction of sodium metal and hydrogen. (This statement is not to be construed as meaning that equation (F) is not valid. Given proper agitation to expose fresh surfaces of sodium metal, copious quantities of sodium hydride may be thus produced.)

In a search for clues to the behavior of the reactants at higher temperatures, several experiments were made utilizing only one of the primary reactants in combination with one or more of the reaction products. (e.g., sodium metal or hydroxide with sodium hydride). The data from these experiments are shown in Figures 10 and 11. As may be seen sodium metal with sodium hydride follows the true dissociation curve for sodium hydride until a point is reached where the amount of sodium present will dissolve all the remaining sodium hydride with a resulting stabilizing effect. (Figure 10). (This type of data will be presented in a later report on the solubility of sodium hydride in sodium metal.) No deviation from the dissociation pressure data at 190mm, such as was noted in sodium-sodium hydroxide runs, was found. However, if sodium metal, sodium hydride and sodium oxide are heated together, the type of curve obtained is similar to that obtained for sodium-sodium hydroxide. (see Figure 10) Again, there is no break at 190mm where large amounts

of sodium hydride are involved. The leveling off of the pressure and reabsorption of hydrogen is quite apparent, however.

If sodium hydroxide and small amounts of sodium hydride are heated together the data conforms to the dissociation pressure of sodium hydride for a short time and then breaks away, levels off and then climbs slowly until all hydride hydrogen is recovered. (Figure 11) (Note -- no further hydrogen was developed indicating that the sodium metal had been removed from the reaction zone.) Large amounts of hydride show continued evolution of hydrogen. There is a tendency to level off near 175mm, but this is overcome with increasing temperature. A run made with sodium monoxide added, however, exhibits a sharp break at 195mm and 425°C, leveling off completely at this point. Further heating causes a slight absorption and eventual re-evolution of hydrogen at 525°C. Sodium monoxide is thus shown to be the key to the reabsorption of hydrogen in the 425° to 500°C range. It is also indicated that both sodium monoxide and sodium hydroxide must be present to cause the cessation of H_2 evolution at ca 190mm pressure. It is probable that they also must be present in some definite proportion. It should be noted that the pressure at which runs first level off (10mm, 35mm, 140mm) is almost exactly 1/2 of the total pressure available if secondary reaction with sodium metal is eliminated. It is quite doubtful if this secondary reaction was eliminated in runs containing any considerable amount of sodium hydride. The second of the plateaus in the run involving .856 gram of NaH is ascribed to the reaction of sodium with sodium hydroxide in an amount sufficient to produce enough sodium monoxide for the indicated reabsorption of hydrogen. The significance of the plateaus at 1/2 of the available pressure is not apparent. Similar data were obtained in nearly all sodium-sodium hydroxide runs in which the hydrogen was pumped away after the first equilibrium and new equilibrium pressures obtained which often were almost exactly 1/2 of the preceding pressure. The best explanation is one of an equilibrium pressure depending upon concentration of solute, dilute solutions having lower equilibrium pressures with a subsequent tendency toward the 1/2 way point. This same condition could also determine the point of deviation from sodium hydride dissociation pressure data as well as the peak pressures obtained for concentrations up to that required to give 190mm.

Another run involving reaction products was made in which sodium monoxide was heated to 550°C, (the point of minimum pressure on the sodium-sodium hydroxide curve) increments of hydrogen added, and equilibrium points observed. Even at this temperature the reaction proceeded according to the equation



The data plotted in Figure 12 gives weight to those points representing "dead stops" as true equilibrium points. The time element occasionally prevented complete absorption of a particular addition of hydrogen before a days run was terminated. As is shown in the graph the monoxide exhibits a linearly increasing equilibrium pressure until a pressure of ca 175mm is reached. The continued addition of hydrogen beyond this point results in a plateau and finally a decreasing equilibrium pressure as the ratio of sodium hydroxide and/or sodium hydride to sodium monoxide increases rapidly. The final point was obtained by pumping away excess hydrogen until sodium hydride in the melt began to decompose. All excess hydrogen pressure was then removed (130mm) and the melt allowed to again equilibrate. A total of 170mm of hydrogen pressure was removed in this manner at 550°C. At this point no further evolution of hydrogen was observed. The heat was turned back and the cooling curve observed. Only 5mm additional hydrogen was given off in cooling through 250°C. Upon reheating through 450°C another 7mm was evolved. After cooling to room temperature, the residue was hydrolyzed in a closed system and hydrogen equivalent to the remainder of the sodium hydride was collected. The quantity of sodium hydride remaining before hydrolysis was equivalent to ca 20% by weight, of the residue. It appears likely that this is the value for the solubility of sodium hydride in sodium hydroxide at 550°C, and that once in solution at that temperature it is quite stable -- even under high vacuum.

A sodium oxide-hydrogen reaction carried out at 360°C does not exhibit the phenomena discussed above. At this temperature, the reaction proceeds in such a manner as to repeatedly come to equilibrium at ca 100mm pressure of hydrogen. This pressure is nearly exactly what would be predicted from sodium hydride dissociation pressure data. Evidently the hydride formed is not in solution at this temperature. It is probable that the "melt" contains no liquid phases, but is a mixture of 2 or more intermixed solids in contact with the gas phase.

From Figure 12 it would appear that the equilibrium pressure of hydrogen over a mixture of sodium monoxide-sodium hydroxide-sodium hydride and perhaps some sodium metal is dependent largely upon the amount of sodium monoxide present or upon the ratio of sodium hydroxide to sodium monoxide. The ratio of sodium hydroxide to sodium hydride is assumed to be mole for mole (or 37.2 weight percent) sodium hydride in sodium monoxide for the complete run whereas the quantity of sodium hydroxide is being constantly depleted. The point at 175mm where the curve breaks, flattens and eventually curves downward appears to be the result of the disappearance of all solid phases in the system -- i.e., complete solution of all reactants

in sodium hydroxide. Figure 13 gives further evidence that this is the case. The data plotted in that figure is a determination of the solubility of sodium monoxide in sodium hydroxide or, more properly, a determination of the fusion temperature of various ratios of the two. It was determined in air in a nickel crucible by adding weighed portions of sodium monoxide to fused hydroxide until saturation became apparent by the appearance of solid oxide on the surface of the melt. It may be noted that the solubility value at 550°C is 48%. Calculation of the ratio of sodium monoxide and sodium hydroxide at the 175mm break point in figure 12 reveals that the sodium monoxide amounts to 45 weight percent of the melt with respect to sodium hydroxide. At this point, therefore, the melt became fluid. The previously determined stability of sodium hydride in solution and continuing reduction in the quantity of sodium monoxide having the effect of making the solution of sodium hydride in sodium hydroxide less concentrated even though their ratios remain the same would readily account for the downward trend of the equilibrium pressure at the end of the curve. The inability to recover all hydride hydrogen by evacuation is explained by the increased melting point of the concentrated melt (6) resulting in the hydride being completely soluble at the temperature of fusion. It is considered to be more than coincidental that the breaks in the solubility curve shown in Figure 13 occur at 380°C and at 425°C. These same temperatures represent the points of deviation from sodium hydride dissociation pressure data and the point of maximum pressure respectively in any sodium-sodium hydroxide reaction curve. The area between the two temperatures, therefore, must represent a rapidly changing condition of the melt, with a final disappearance of all solid phases at 425°C.

Miscellaneous data has, of course, been gathered during the course of this investigation.

Time-pressure relationships for some of the reactions reported is perhaps noteworthy. Representative data for typical runs are presented in Figure 14.

A study involving attempts to duplicate the sodium-sodium hydroxide data with potassium metal and with sodium-potassium alloys is of comparative value. Sodium metal and any alloy of sodium and potassium containing sufficient sodium to complete the reaction will react with either sodium or potassium hydroxide to give equilibria exactly as has been presented in this paper. However, potassium metal with either sodium or potassium hydroxide will not produce such equilibria. As is shown in Figure 15 these materials will react to give some hydrogen at temperatures between 450-600°C. The yield of hydrogen is low and even with continued removal of the hydrogen evolved, complete conversion to potassium monoxide was never accomplished. Something similar to this reaction, or rather lack of reaction may be added to the difficulty reported by Holt (9) in his attempt to apply the method for hydrogen determination in sodium to sodium-potassium alloys.

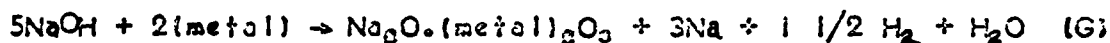
A somewhat more complete discussion of the high temperature reaction between sodium hydroxide and the stainless steel "pot" might be of value. The reaction occurred at temperatures in excess of 600°C and was accompanied by the evolution of both hydrogen and water vapor, the latter being condensed in a cold trap attached to the system. This is in agreement with results reported by LeBlanc and Bergman (10). Metallic sodium was also found condensed upon the colder portions of the metal system when it was cut open for residue recovery. The analysis of this residue is shown in Table I.

TABLE I

Na ₂ O	27.6 weight percent
Na ₂ CO ₃	1.2
Fe ₂ O ₃	57.0
Cr ₂ O ₃	6.3
NiO (?)	7.1

The oxides of chromium and iron were identified by their appearance and by physical and chemical behavior during analyses. The state of the nickel could not be determined with certainty.

The presence of metallic sodium, hydrogen, water, sodium monoxide and the metal oxides in the reaction products indicate that the reaction must have proceeded in somewhat of the following manner.



The existence of the water vapor was of a transitory nature. It was apparently driven from the reaction zone by the high temperature, and immediately condensed in the cold trap. When the system was allowed to equilibrate without the cold trap, the water was removed by reaction with the metallic sodium.

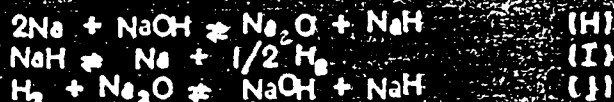
The double salt indicated is a postulation and was not identified as such in the residue. Such salts have been previously reported (10), however, and sodium ferrite and chromite of the form $\text{Na}_2\text{Me}_2\text{O}_4$ are relatively well known.

The residue from the run involving sodium hydroxide and the nickel "pot" contained only a trace of nickel, probably coming from surface oxides on the "pot".

SUMMARY

From the data presented, it seems clear that sodium metal will react with sodium hydroxide at temperatures over 300°C

yielding sodium monoxide and sodium hydride, both of which are potentially stable in the melt. If the reaction occurs under as little as 200 mm of any gas pressure the hydride dissociation will be suppressed sufficiently to maintain it in solution, even at a temperature of 600°C. The system appears to be influenced by a number of simultaneous reactions illustrated by the following equations:



These reactions, coupled with various solubility or phase changing effects, determine the equilibrium.

The point of maximum pressure in the system is apparently determined by the ratio of sodium hydroxide to sodium monoxide and is influenced by the amount of sodium hydride. The effect of sodium metal upon this point is negligible except for the relatively small solubility of sodium hydride in the metal. The reabsorption of hydrogen by the system at higher temperatures requires the presence of sodium monoxide and is brought about by the increased solubility of sodium hydride in sodium hydroxide, and the more fluid nature of the melt.

The dissociation of sodium hydride has been shown to be considerably suppressed by inert gas pressures as low as 190 mm. To the knowledge of the author this phenomenon has not been previously reported. This fact alone has considerable bearing on corrosion problems involving sodium metal or sodium hydroxide. It has previously been supposed that sodium hydride would dissociate and be removed from reaction areas. This is evidently not true, and the action of this compound, particularly on metal oxides in the system, could result in considerable corrosion.

Several attempts to apply the phase rule to this system were unsatisfactory. It can be applied with confirmatory results by arbitrary selection of phases and/or components. The author can see no value in reporting such calculations until such time as more definite evidence as to the true state of the various equilibria in this system can be determined. It seems evident from the data presented that an equilibrium does exist with at least one quasi-equilibrium having a contributory effect.

The data herein contained are felt to be reasonably conclusive per se, but further work is indicated in the direction of establishing the true phase diagram for such a system. The answer might be found in a melting point type of investigation but this venture, too, is fraught with errors of interpretation until a means is found to analyze the melt at the temperature being studied.

While the mechanism of corrosion is beyond the scope of this report, there is a definite effect indicated which should bear upon future investigation and argues for a more careful evaluation in using past data.

REFERENCES

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ILLUSTRATIONS
FOR
NRL MEMORANDUM REPORT NO. 33

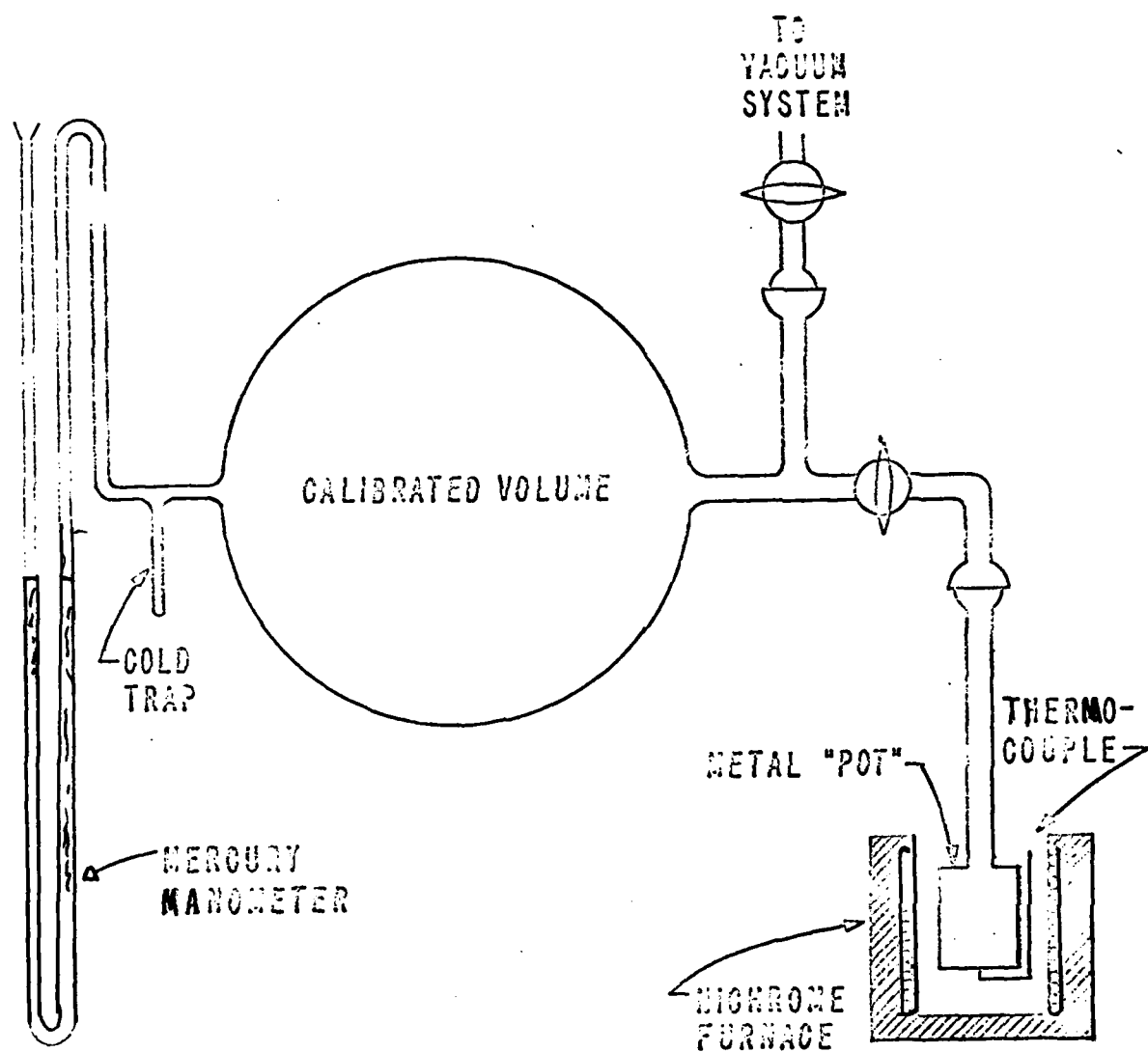


FIG. 1 APPARATUS FOR THE STUDY OF THE SODIUM-HYDROGEN-OXYGEN SYSTEM

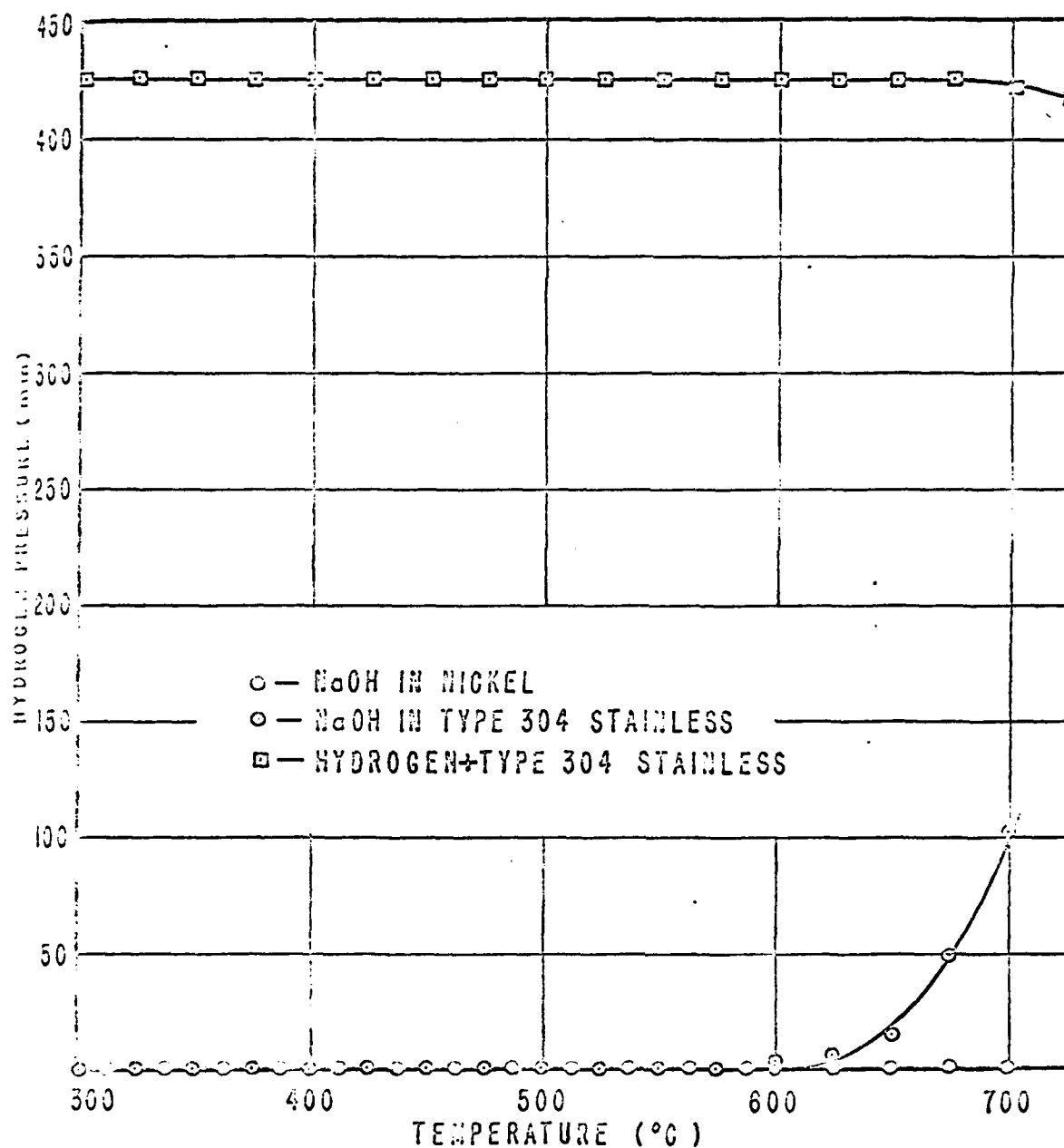


FIG. 2 EFFECT OF SODIUM HYDROXIDE AND HYDROGEN ON "POT" MATERIALS

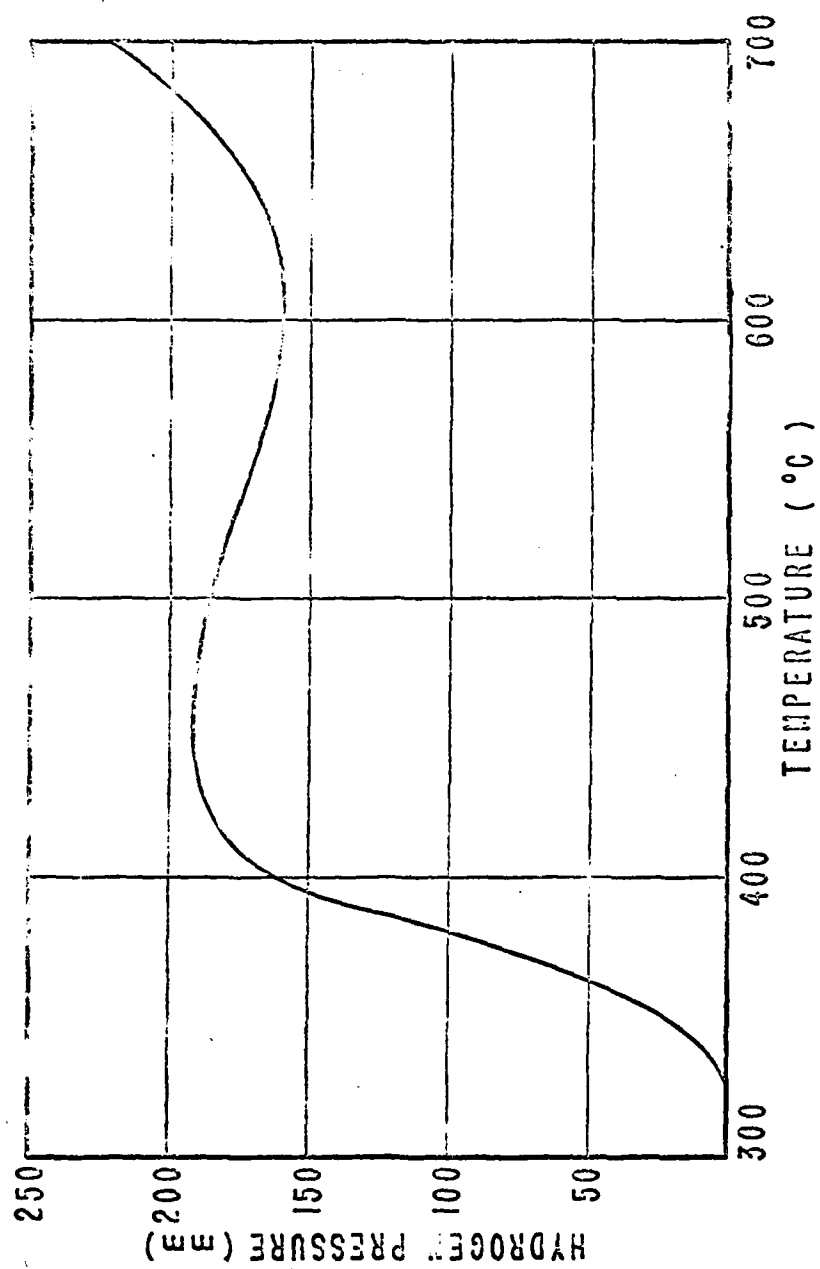


FIG. 3 TYPICAL SODIUM - SODIUM HYDROXIDE REACTION CURVE

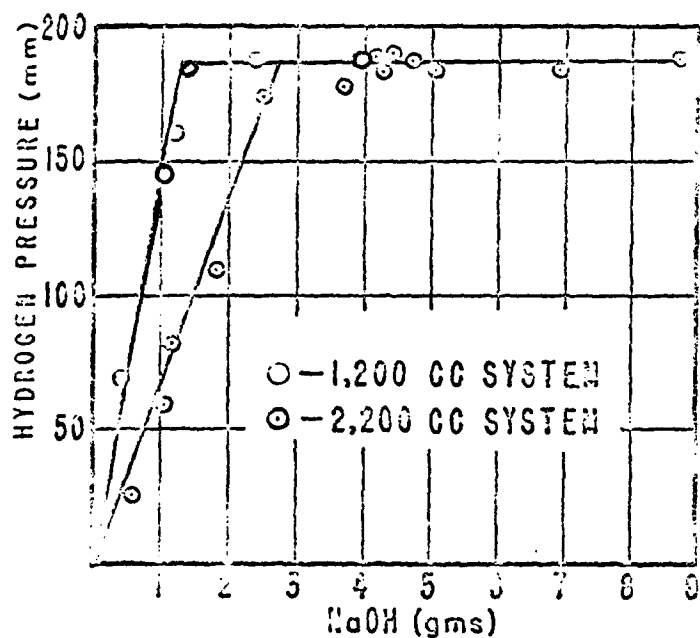


FIG. 4 EFFECT OF SODIUM HYDROXIDE ON
 PEAK PRESSURE AT 425° C

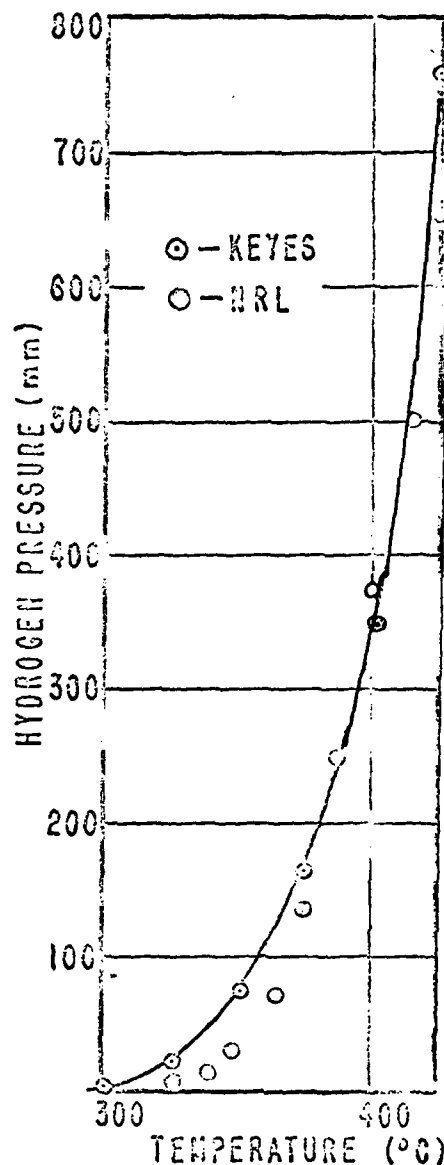


FIG. 5 DISSOCIATION PRESSURE
 OF SODIUM HYDRIDE (IN VACUO)

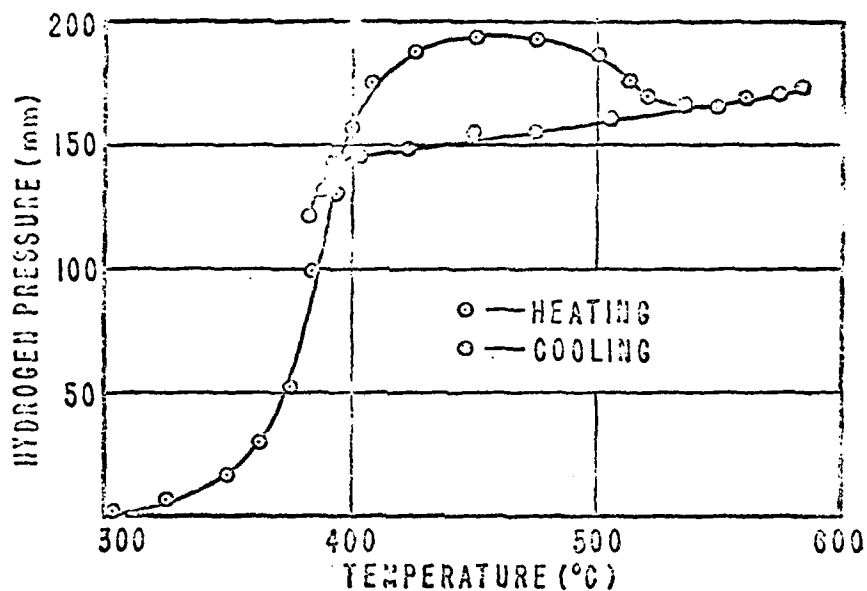


FIG. 6 QUASI-EQUILIBRIUM IN SODIUM-SODIUM HYDROXIDE REACTION

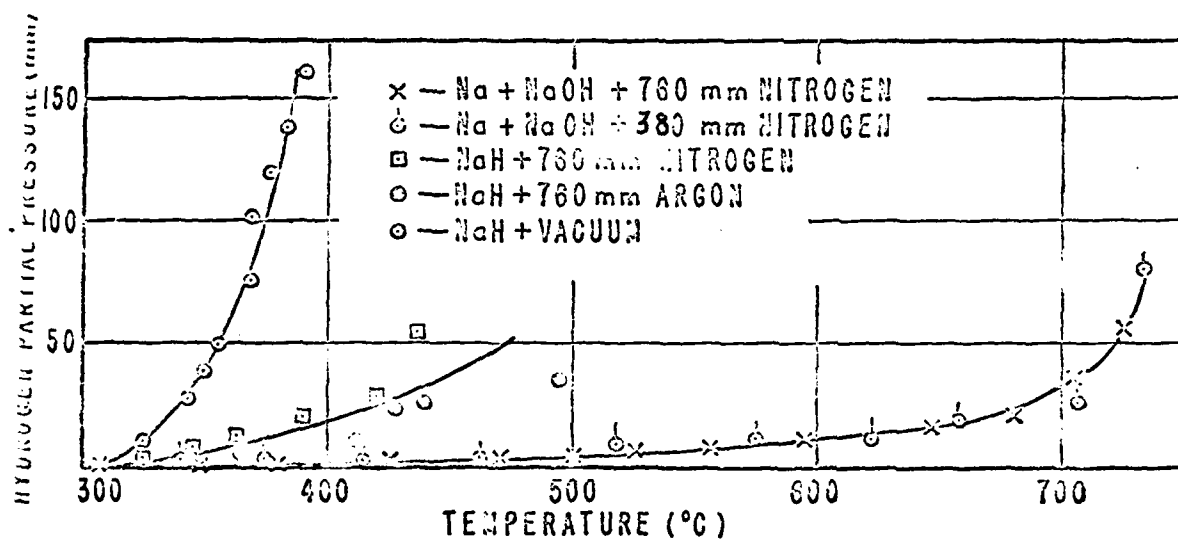


FIG. 7 EFFECT OF INERT GAS PRESSURE UPON THE SODIUM-SODIUM HYDROXIDE REACTION AND THE DISSOCIATION OF SODIUM HYDRIDE

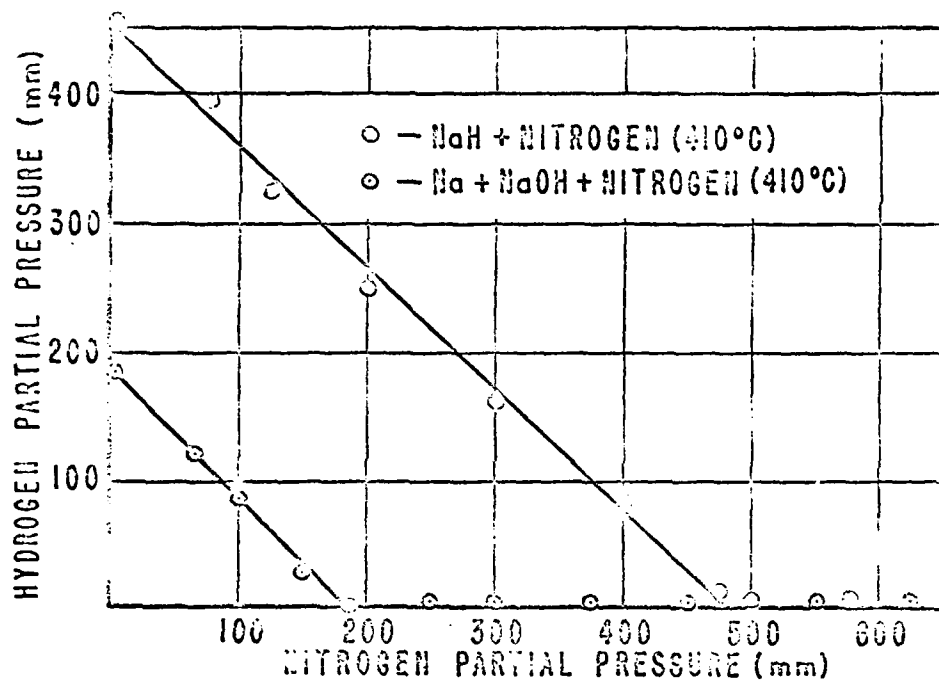


FIG.8 NITROGEN-HYDROGEN PARTIAL PRESSURE RELATIONSHIP OVER SODIUM - SODIUM HYDROXIDE & OVER SODIUM HYDRIDE

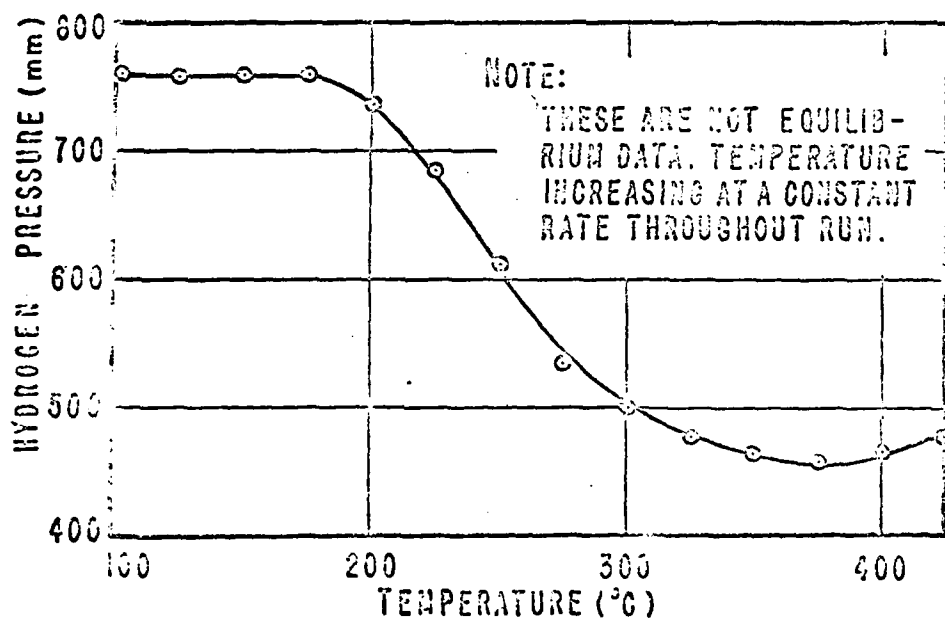


FIG.9 REACTION OF SODIUM MONOXIDE WITH HYDROGEN

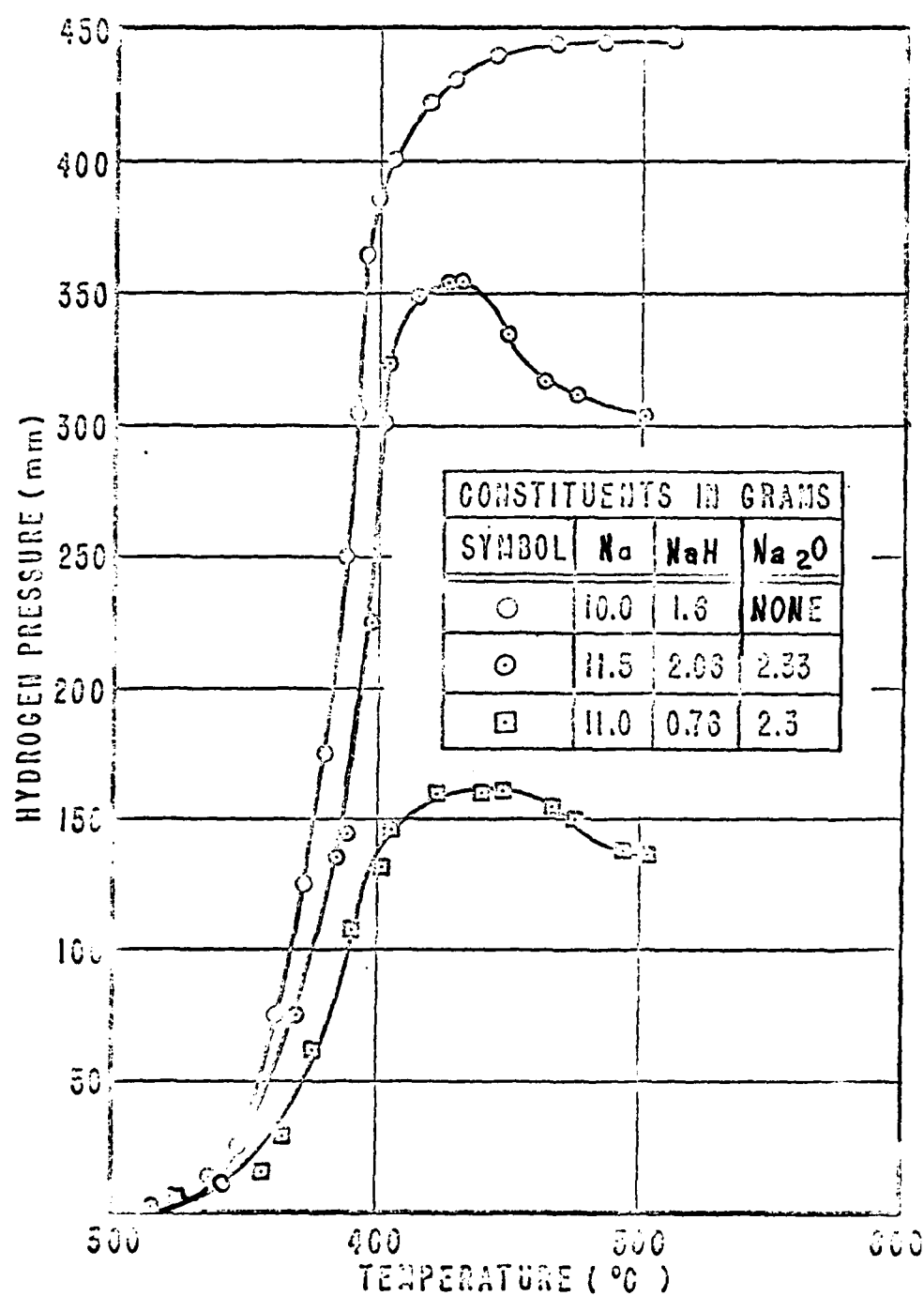


FIG.10 THE SODIUM - SODIUM OXIDE - SODIUM
HYDRIDE SYSTEM

(H₂ PRESSURE X 1.45 = c.c. H₂)

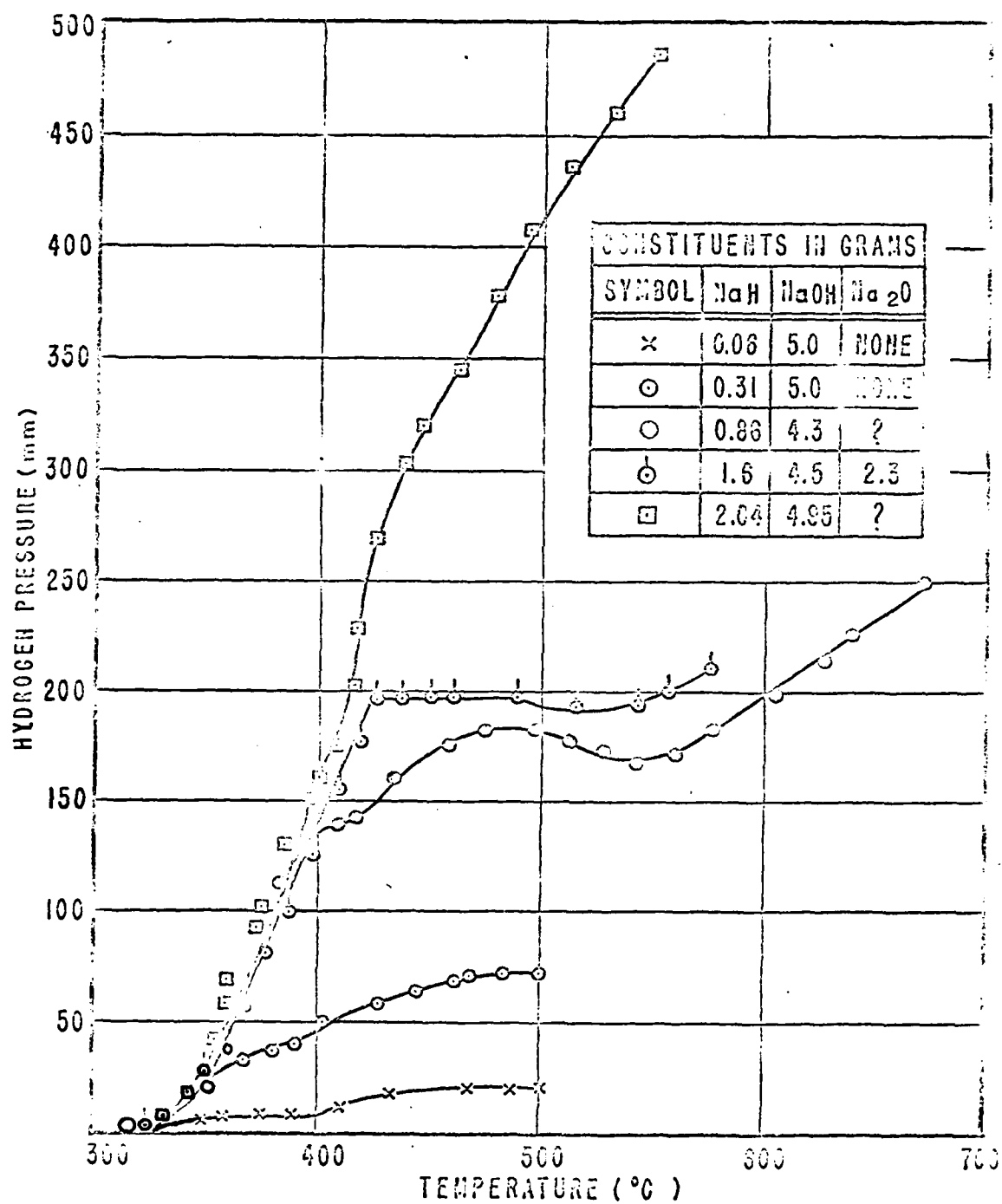


FIG. 11 THE SODIUM HYDROXIDE-SODIUM HYDRIDE - SODIUM OXIDE SYSTEM

(H₂ PRESSURE X 1.45 = C.C. H₂)

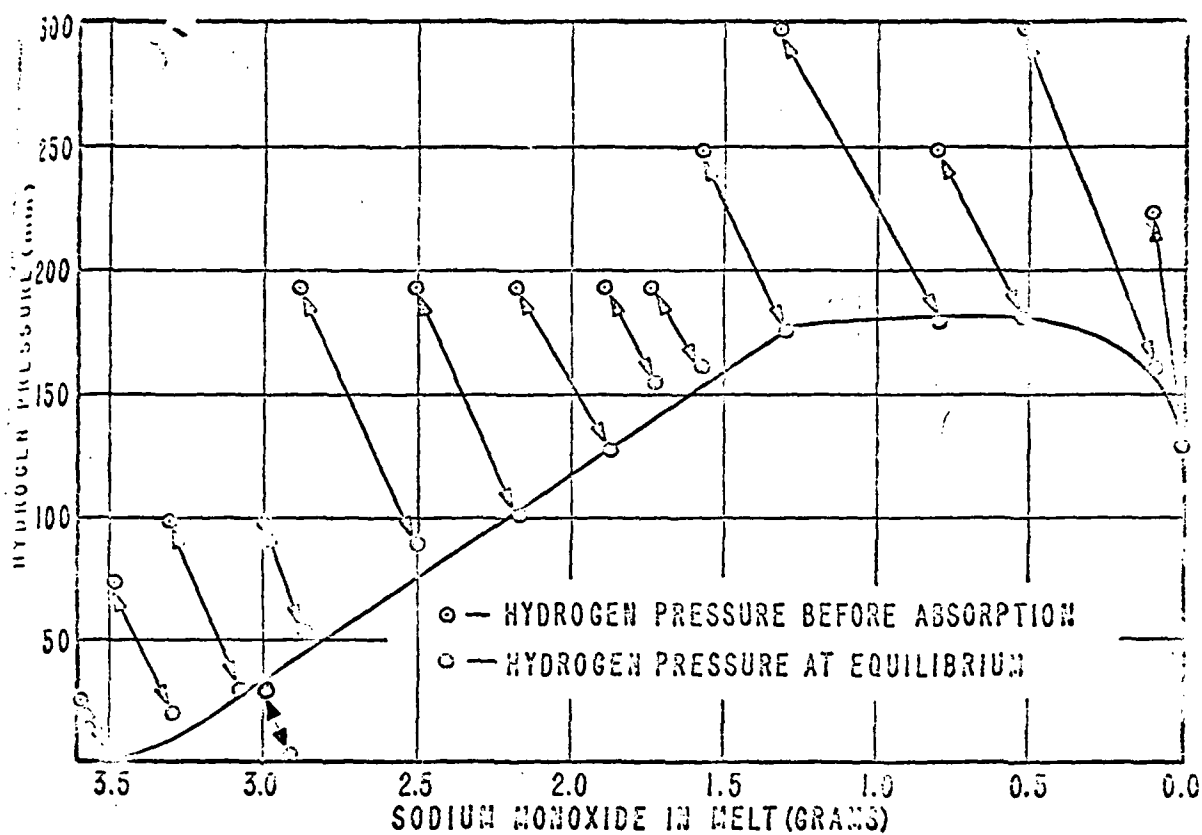


FIG. 12 REACTION OF SODIUM MONOXIDE WITH HYDROGEN AT 550°C
(H_2 PRESSURE $\times 1.45 =$ c.c. H_2)

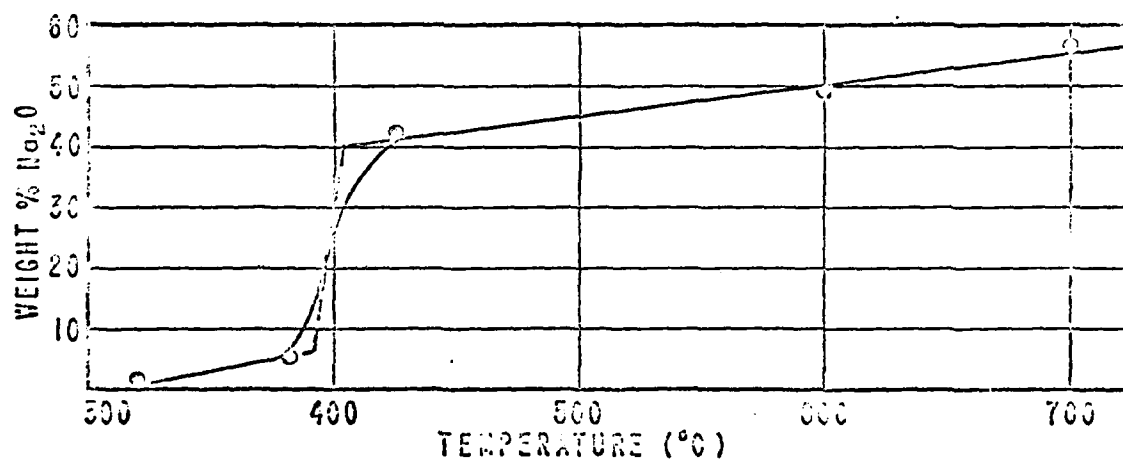


FIG. 13 SOLUBILITY OF SODIUM MONOXIDE IN SODIUM HYDROXIDE

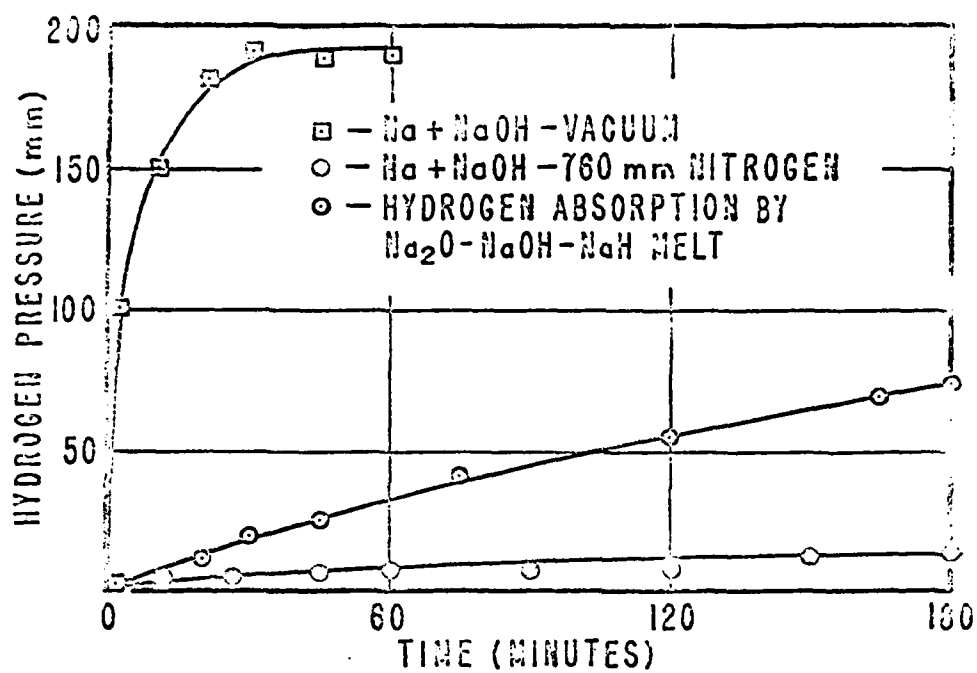


FIG.14 EQUILIBRIUM RATES AT 410°C

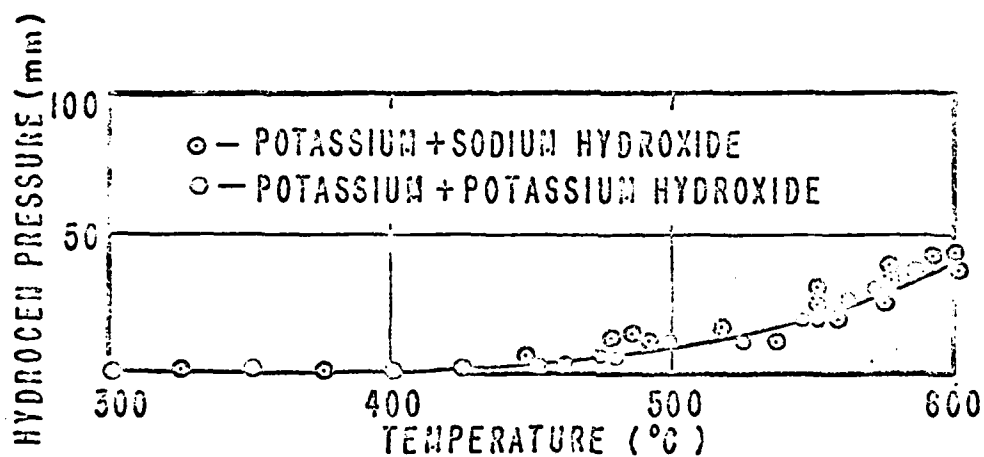


FIG.15 COMPOSITE DATA FOR POTASSIUM-HYDROGEN-OXYGEN SYSTEM